

IMPROVED SEPARATORS FOR SILVER OXIDE-ZINC
AND SILVER OXIDE-CADMIUM CELLS
FOR SPACECRAFT APPLICATION

by

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Errata

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- On page 7, second paragraph, last line - delete 1965
- third paragraph, line 2 - effect should read effect
- On page 12, in Table IV - solubility should be solubility
- On page 17, in Table VIII - the original resistance of the last film (522-140) should be 34.8, not 34.8
- On page 23, in Table XII, - the composition column should read:

C-3
MS + NaOH
C-1 + lactate
MS + KOAc
MS + KOH

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PROJECT PERSONNEL

In carrying out the experimental work herein reported, the writers were assisted at The Borden Chemical Company by Dr. George Kitazawa, Head of the Physical Testing Laboratory, Mr. Richard Trickey, Chemist and by Messrs. Ronald G. Burton and S. Weeks, Assistants. At the Carl F. Norberg Research Center of the Electric Storage Battery Company, the subcontract tests were supervised by Mr. J. Kelley.

INTRODUCTION

This is the Third Quarterly Progress Report under NAS-5-9107, Modification 6. Among the subjects discussed herein are experiments improving the conductivity of methyl cellulose membranes by precooling in aqueous alkali, or by pre-soaking in alkali solutions less concentrated than those to be used in the battery cell, as well as by formulating with various polar additives including tetramethylammonium hydroxide. Certain acrylic copolymer systems have been prepared as candidates for improved battery separators. Other work in progress includes multiple wraps with alternating layers of different types of membrane.

SUMMARY & CONCLUSIONS

1) Physical modifications of methyl cellulose membranes to more permeable structure was accomplished by precooling at below -55°C . and by presoaking in KOH concentrations below those used in the cell.

a) Precooling a methyl cellulose membrane at below -55°C . in 30% KOH lowered the resistance of the membrane at room temperature from 590 milliohms-in.² to an average of 60 milliohms-in.² The low resistance persisted over a 134 day period. Increased swelling and increased diffusion rate for silver accompanied the resistance change.

b) Presoaking methyl cellulose membranes in 15% KOH lowered the resistance in both 30% and 45% KOH and likewise increased swelling and permeation to silver ion.

2) Application of these permeabilization procedures to methyl cellulose compositions with polar additives resulted in a wide range of electrolytic resistance. Certain films had resistance lower than cellophane; although silver diffusion rate would be too high for use in Ag/Zn or Ag/Cd cells, such films might have application in other types of cells.

3) Experimental cells are under test at Electric Storage Battery Company in which the electrodes are wrapped with alternating layers of different types of membrane. One type is predominantly polyvinyl alcohol and designed to stop silver by chemical action. The other type is predominantly methyl cellulose resistant to silver oxidation and penetration by zinc metal. Membranes of half-thickness (0.8 mil) were prepared for this assembly.

4) The tendency of membranes to crack at the U bend is being studied. Preliminary experiments were carried out on applying plasticizer, including the electrolyte, at the area of stress.

5) C3 film cast from solutions buffered with KOH to pH 8 has resistance in 45% KOH lowered from about 500 milliohms-in.² to 19 milliohms-in.² This was accompanied by a threefold increase in the average silver diffusion rate. However, practicality of these buffered films is limited by difficulties in their manufacture.

6) A battery of cells prepared with C3 separator was charged three times and held for stand-time periods before discharge of 76, 104 and 174 days. Capacity was reduced to an average of 90%, 70% and 28% of nominal after the respective stand times.

7) The effect on resistance of long exposure (3 to 18 months) of representative membranes to soluble silver oxide in 30% KOH was found to be relatively minor. This was true even with readily oxidizable films such as cellophane and polyvinyl alcohol which show high loss in strength.

8) Copolymers of methacrylate esters with acrylic acid were prepared by selective hydrolysis of the corresponding esters. Compositions up to 45 mole % of acrylic acid were prepared. These gave typically brittle films. Neutralization in part or completely with bases gave more flexible films capable of being handled. Resistance values on one preparation were below those of cellophane in 30% KOH, somewhat higher than cellophane in 45% KOH. Silver diffusion rates were correspondingly high.

9) A methyl cellulose composition incorporating 10% tetramethyl ammonium hydroxide on the polymer gave resistances in 45% KOH of from 45 to 62 ohms-cm on four replicate preparations and MIT Flexes of 4000 to 7000 cycles. Performance in experimental Ag/Zn cells at Norberg Research Center was good.

10) Electrolytic resistances of selected films were measured in concentrated KOH saturated with Zinc oxide. In 45% KOH, resistances were in some cases increased considerably over the corresponding resistances in ZnO-free electrolyte.

DATA & DISCUSSIONA. Modification of Methyl Cellulose Membranes by Pre-Cooling

The observation that heating a methyl cellulose film at 80° C. in 45% KOH increases its electrolytic resistance suggested that pre-cooling in electrolyte might have the opposite effect. Experiments have shown that this is indeed the case. For these experiments 30% KOH was chosen because of its low freezing point, and a bath temperature of 55-60° C. below zero was maintained with dry ice and isopropanol. This was just short of the freezing point of the electrolyte. Following the cold treatment, the 30% KOH was warmed to room temperature and the resistance of the films measured in duplicate, with the results shown in Table I.

TABLE I. - Effect of Pre-Cooling Methyl Cellulose Films (1.5 mils)
on Electrolytic Resistance

	Expt. No. 562-	7	9	11	21	482- 136	Control MC at Room Temp.
Time of soak at 25° C. hrs.		0	19	0	0	0	
Pre-cooling at -55° C. to -60° C. hrs.		6	6	7	6	2	
Resistance - ohms-cm 25° C.							
4 days		33.2	-	*	47.4	78.6	498
11 days		-	-	-	-	-	-
24 days		-	-	52.1	-	-	-
31 days		-	-	-	-	-	-
46 days		41.0	69.4	-	-	-	-
68 days		-	49.8	-	-	-	-
90 days		-	-	-	49.7	-	-
134 days		-	66.0	-	-	-	-

* Used in silver diffusion tests.

The large lowering in resistance was accompanied by a corresponding increase in the permeability to dissolved silver. As reported in the Second Quarterly Report, the average rate of diffusion of silver ion through the membrane increased from 0.24% to 4.5% per day, expressed in units of percent of the silver charged to one side of the membrane

The membrane is swollen by the cold treatment. This was shown by amount of 30% KOH imbibed after standing at room temperature for three days. The weight gain was 88% compared to 25% observed for the membrane when equilibrated directly in 30% KOH without the pre-cooling treatment.

The efficacy of low temperature treatment is related to the unusual solubility characteristics of methyl cellulose which is insoluble (gelled) by hot water but soluble in cold water.

The principle of pre-cooling was applied to a B3.3 film (33% polyacrylic acid, 67% methyl cellulose). Here also a marked reduction in resistance occurred in 30% KOH as shown below. Very little effect was found in 45% KOH.

TABLE Ia. Effect of Temperature History on Resistance of B3.3 Film

Conditions		Resistance ohms-cm
30% KOH	3 days at 25° C.	26.4
30% KOH	9 hours at -56° C., 3 days at 25° C.	6.5
45% KOH	4 days at 25° C.	654.
45% KOH	8 hours at -58° C., 4 days at 25° C.	548.
45% KOH	9 hours at -27° C., 4 days at 25° C.	588.

The resistance value for pre-cooled B3.3 film (33% PAA, 67% methyl cellulose) in 30% KOH is identical to the experimental value found here for PUDO cellophane.

The most dramatic reduction in resistance was found in pre-cooling a methyl cellulose film which was cast from a dilute KOH solution incorporating 9% KOH on the polymer. In 30% KOH the film was greatly softened, showing a tendency to stick to itself. Resistance was lowered from 74.6 ohms-cm to 1.6 ohms-cm.

Although silver diffusion data on the pre-cooled B3.3 and MC + 9% KOH films were not obtained a high rate would be predicted on the basis of the correlation of silver diffusion rate with resistance observed in the work of the Second Progress Report. A film in this resistance range might not, therefore, be suitable for a silver-zinc cell, but might show advantageous properties in other cells, as for example oxygen/zinc.

A practical method of applying the pre-cooling principle in battery cells would be to assemble the cell as usual with dry membrane, then add electrolyte and cool the entire cell in a cold box. Time was not available to include this procedure under the present Contract. In further exploitation of this approach, it would be desirable to study a range of cooling temperatures. The possibility should be examined of obtaining similar effects under less severe cooling conditions by strategic combination of KOH-incorporation and cooling. In using the KOH-incorporation approach without cooling it is desirable to go up to 9% KOH level. If cooling is carried out at -55°C. , even 0.5% KOH-incorporation leads to excessive swelling. In order to establish the optimum range of pretreatment conditions, films representing a range of KOH-incorporation should be treated in a range of concentrations of concentrated KOH over a range of temperatures and exposure times.

The fact that the properties of methyl cellulose type films are affected by exposure to cold alkali must be kept in mind in their application in battery cells. For example, in space applications temperature control should be adequate to maintain all film properties including electrolyte resistance within desirable limits.

B. Modification of Films By Pre-Swelling in 15% KOH

As reported in the Final Report of previous Contract, and on page 15 of the First Progress Report, when methyl cellulose is pre-swollen in 15% KOH, then equilibrated in 30% or 45% KOH, resistances in the stronger electrolytes are of the same order as obtained for methyl cellulose films modified with polar mixtures. A practical method of exploiting this property of methyl cellulose would be to wrap electrodes or electrode forms with methyl cellulose, condition these first in 15% KOH, then equilibrate the assemblies in electrolyte of the concentration employed in the cell.

The procedure was extended to include compositions of methyl cellulose with polar additives. As was anticipated, resistances were lowered still further, in some instances to values below that of cellophane. The degree of permeability obtained may be too great for the silver-zinc cell but could be of interest for other systems. The results of several such pre-swelling experiments are given in Table II. Silver diffusion experiments on pre-swollen methyl cellulose were reported in the Second Quarterly Report, 1965.

The major mechanism operating in the pre-soaking procedure is believed to be the solvating effect of the dilute KOH. However, qualitative tests on the 15% KOH liquor after swelling did show the presence of organic matter, so that the enhanced conductivity could be derived in part from a leaching action by the more dilute KOH.

TABLE II. - Effect of Pre-Swelling Films in 15% KOH on Resistance
in 30% and 45% KOH

	MC	C1	C2	B2	B3.3	MC + 33% KOAc
	485-118	421-116	421-102	522-105	504-29	534-63
Dry Thickness - mils	1.5	1.5	1.5	1.5	1.5	1.5
Swollen Thickness - mils						
Directly in 30% KOH	1.88	2.10	2.13	2.3	2.3	1.8
15% → 30% KOH	2.44	2.0	2.3	2.6	2.8	3.1
Resistance - ohms-cm						
Directly in 30% KOH	498.	71.2	22.6	152.	26.5	28.1
15% → 30% KOH	17.3	10.3	9.1	6.7	2.9	4.8
Dry Thickness - mils	1.5	1.5	1.5	1.5	1.5	1.5
Swollen Thickness - mils						
Directly in 45% KOH	1.83	2.07	2.28	1.9	2.1	1.74
15% → 45% KOH	2.52	2.30	2.20	2.8	2.8	3.1
Resistance - ohms-cm						
Directly in 45% KOH	6080.	905.	738.	635.	574.	53.8
15% → 45% KOH	60.	11.2	7.4	9.5	4.5	5.6

NOTES: MC Methyl Cellulose
 C1 10% PVMA/90% MC
 C2 20% PVMA/80% MC
 B2 20% PAA/80% MC + KOH to pH 5
 B3.3 33% PAA/67% MC + KOH to pH 4

C. Methyl Cellulose Plus Organic Bases

The use of inorganic and organic bases to enhance the conductivity of methyl cellulose was described in the Final Report of previous Contract. The investigation was extended to include the quaternary ammonium bases, tetramethyl and tetraethyl ammonium hydroxide. These showed to advantage over formulations earlier reported, giving lower resistance as well as good flexibility.

A formulation with tetramethyl ammonium hydroxide showed superior performance in experimental cells at Norberg Research Center as NRS 5-9107-27 (see Final Report).

Properties of the films are summarized in Table III in comparison with a typical C3 film, with previous formulations with higher molecular weight quaternary ammonium hydroxides, and with a formulation with KOH.

Table III. - Formulations of Methyl Cellulose with Hydroxide Bases

Reference	Base	Base % on MC	Elec. Resist. ohms-cm		MIT Flex 50% R.H. Cycles	Tensile 50% R.H. psi	Thickness Dry mils
			30% KOH	45% KOH			
545-64	Me ₄ NOH	10	29.2	46.7	5,295	6,640	1.5
545-20	Et ₄ NOH	10	46.8	278.	-	-	1.5
545-21	Et ₄ NOH	20	15.2	69.	-	-	1.5
504-139	BzMe ₃ NOH	10	-	1,820.	4,745	-	1.5
499-15	C3	-	16.0	503.	754	14,700	1.5
522-62	KOH	9 *	55.	66.9	7,926	4,760	1.5

D. Buffered C3 Films

The pH of the solution from which C3 film is customarily cast is 2.8. Calculation shows that this corresponds to sufficient acidity to lower the electrolyte concentration in a tightly packed cell from 30% to 25%. It was therefore pertinent to study the effects of KOH additions to the casting solution. Films cast from solutions buffered to pH 6 and pH 8 respectively were found to have resistances in 45% KOH of 33.8 and 18.8 milliohms-in.² as compared to 503 milliohms-in.² for customary unadjusted C3 at pH 2.8. The lowered resistances were accompanied by increased silver diffusion from 1.9% per day to 5.4% per day, expressed in arbitrary units of percent of the silver initially charged to one side of the membrane.

Films cast from buffered solutions had a disadvantageous tendency to fissure on drying. No drying method was found to prevent the fissuring tendency. The condition was corrected by including 5% on polymer of either tetraethyleneglycol or triethanolamine. Films of these compositions were submitted as NAS-9107-31 and -32 for testing in experimental cells at Electric Storage Battery Company. As will be reported in the Final Report under this Contract, performance was not satisfactory.

E. Methacrylic Ester/Acrylic Acid Copolymers

Continuing earlier reported work on these compositions (1)(2), several copolymers were prepared according to the schematic in Figure 1.

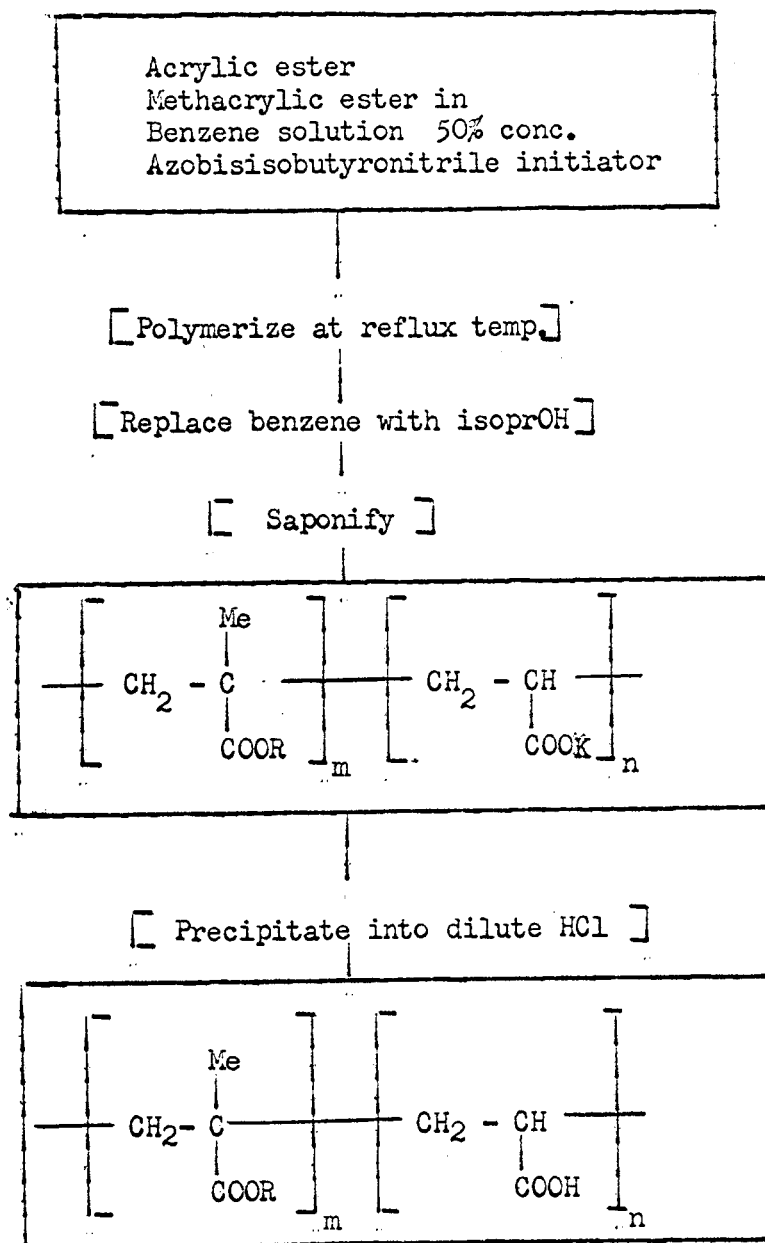


Figure 1

Schematic for Preparation of Acrylate Compositions

Compositions were determined by elementary analysis and by titration, with fairly good agreement being obtained. Preparations by the method are given in Table IV.

TABLE IV. - Methacrylic Ester/Acrylic Acid Copolymers
(Solution Polymerization in Benzene)

Prepn.			Polymerization Solution - Benzene			Emulsion Polymer
			545-102	563-52	563-74	563-137
<u>Formulation:</u>	Ethyl acrylate	moles	.5	.5	.4	.4
	Methyl methacrylate	moles	.5	-	.6	.6
	Butyl methacrylate	moles	-	.5	-	-
Copolymer Ester		state	solid	semi- solid	solid	solid
Properties Acrylate Ester by Sapon.* Mol. %			42.2	51.4	48.6	32.15
Hydrolysis Product (methacrylic ester/acrylic acid)		state	solid	solid	solid	solid
Solubility	in H ₂ O		sl.s.	sl.s.	sl.s.	insol.
	in aqueous bases		sol	gel	sol	insol
	in isoprOH		sol	sol	sol	insol*.
	C %		55.6	62.03	55.92	57.31
	H %		7.25	8.45	7.15	7.38
	O % (by diff.)		37.15	29.52	36.90	35.31
Combined acrylic acid - Mol %						
	from C		44.0	47.8	33.3	33.7
	from H		30.8	50.8	29.8	34.7
	from O		46.0	49.2	32.0	33.4
Combined acrylic acid by titration			42.3	38.0	46.9	33.6

*Soluble in 95% dioxane-5% water, dimethyl formamide, dimethyl sulfoxide

The solution polymers in the acid form were solids of high softening points and gave brittle films when cast from polar organic solvents. As is evident from the preparative method they were only slightly soluble in water. The methyl methacrylate/acrylic acid copolymers were completely soluble in water when an equivalent of base was added and it was possible to cast films from such solutions.

The effect of the type and quantity of base added on the physical properties of the resulting films was explored in some detail in the case of the 485-102 preparations, using as bases KOH, ammonia, 3-hydroxypropylamine and triethanolamine.

Referring to Table V, it can be seen that when ammonia was the sole base the resulting film was too brittle to take up, resembling the unneutralized polymer cast from isopropanol. This may be ascribed to the possibility that such films when completely dry are actually of the same (acid) composition, ammonia having been lost, in the former case, by dissociation and evaporation. Whatever the explanation, the observation was used to control the degree of flexibility of the films by the ratio of permanent (higher boiling), plasticizing amines to ammonia in the solutions from which the films were cast, as shown in the table.

TABLE V. - Films from Poly(methyl methacrylate/acrylic acid) Prepn. 545-102

Ref.	Permanent Base	NH ₃		Resistance		MIT Flex**		Tensile Strength	
		equivs.*	equivs.*	30% KOH	45% KOH	50% R.H.	Cycles	50% R. H.	% Elong.
				ohms-cm		mils		psi	
563-									
37-1	None	2.0	-	-	-	too brittle to recover			
37-2	HPA	1.0	-	7.2	12.4	too soft to test			
37-3	HPA	0.5	1.0	.72	20.5	1.5	2,368	2,390	189
59 (A)	HPA	0.5	1.25	.55	26.5	1.9	451	4,400	22
61	TEA	0.5	1.0	.43	26.5	1.7	5,741	1,960	96
62	KOH	1.0	-	3.1	35.7	1.4	12,566	2,340	35
67	KOH	0.5	1.25	-	47.7	too weak to handle, v. brittle			
PUDO				5.9	9.8	1.0	20,000+	17,300	28
C3				16.1	617.	1.5	754	14,700	9

Notes: * Per acid equivalent in polymer

** 200 g. Tension ASTM

HPA is 3-hydroxypropylamine

TEA is triethanolamine

(A) This film was used in silver diffusion tests (Second Report) in 45% KOH. It showed very low oxidizability. Rate of Ag diffusion 5.8%/day, which correlated with low resistance.

Samples of the films of Table V were set up in 30 and 45% KOH and heated at 50° C. over a period of several days as a measure of stability in KOH. The times required for disintegration are noted in Table V-a.

TABLE V-a.

Preparation	Modifying Base	Time for Disintegration - days	
		30% KOH	45% KOH
563-37-2	3-hydroxypropylamine	4	13
563-59	"	5	14
563-61	triethanolamine	3	8
563-62	KOH	5	12

The rationale of using methacrylate/acrylate copolymers is based on the observation that the methacrylate ester moiety was not measurably saponified under normal saponification conditions whereas the acrylate moiety was readily saponified. Whether the disintegration of the films at 50° C. relates to a slow saponification of the methacrylate moiety or of residual acrylate moiety incompletely saponified in the preparation has not been established.

Attempts to obtain films of acceptable physical properties from the other two copolymer esters of Table V were unsuccessful.

A copolymer acrylate/methacrylate ester was prepared by emulsion polymerization (563-137 of Table IV) with the objective of obtaining a product of higher molecular weight and superior physical properties. The product, unlike counterparts obtained by solution polymerization, showed limited solubility in polar solvents but did respond to selective hydrolysis to methacrylate/acrylic acid product. The product was also different in not being measurably swollen by water. Electrolytic resistance was much higher than on films prepared from polymers by solution polymerization.

F. Effect on Resistance of Saturating Electrolyte with Zinc Oxide

The effect of saturating electrolyte with zinc oxide on the resistance of key films is given in Tables VIa and b. Whereas little effect was observed in 30% KOH, considerable effect was found in 45% KOH, reflecting the greater solubility of zinc oxide in the stronger KOH. Solubilities are respectively 5.8 g/100 ml. and 11.5 g/100 ml. in 30% and 45% KOH.

TABLE VIa. Effect on Resistance of Saturating 30% KOH with ZnO

Reference	Composition	Dry Thickness mils	Resistance milliohms-in. ²		Specific Resistance (Ohms per Swollen Thickness)			
			30% KOH-ZnO	30% KOH	30% KOH-ZnO		30% KOH	
					mils	ohms-cm	mils	ohms-cm
	PUDO Cellophane	1.0	11.2	7.6	3.3	8.3	3.3	5.9
522-119	Cl + 28% K Lactate	1.7	35.3	18.8	1.9	38.0	1.9	20.7
522-62	MC + 9% KOH	1.5	62.9	41.6	1.97	83.3	1.97	55.0
534-105	PVALc (42-88)	1.5	36.1	25.6	2.6	35.2	2.6	25.0
499-65	PVALc (30-98)	1.5	34.0	23.7	3.05	28.3	3.05	18.8
545-62	PVALc 95/PVMA 5	1.5	25.8	16.5	2.8	23.4	2.8	15.0
534-63	MC + 33% K Acetate	1.5	29.6	20.0	1.8	41.8	1.8	28.1
545-64	MC + 10% Me ₄ NOH	1.5	22.0	21.8	1.9	29.4	1.8	29.2
499-15	C3	1.5	18.05	16.1	2.55	18.0	2.55	16.0

TABLE VIb. Effect on Resistance of Saturating 45% KOH with ZnO

Reference	Composition	Dry Thickness mils	Resistance milliohms-in. ²		Specific Resistance (Ohms per Swollen Thickness)			
			45% KOH-ZnO	45% KOH	45% KOH-ZnO		45% KOH	
					mils	ohms-cm	mils	ohms-cm
	PUDO Cellophane	1.0	19.6	11.6	3.1	16.1	3.0	9.8
522-119	Cl + 28% K Lactate	1.7	225.	68.6	2.6	220.	2.6	66.9
522-62	MC + 9% KOH	1.5	340.	244.	2.2	393.	2.2	282.
563-101	PVALc (42-88)	1.6	46.7	29.0	3.2	37.1	3.2	11.6
563-17-6	PVALc (30-98)	1.4	43.9	31.5	2.4	46.5	3.45	23.1
545-62	PVALc(42-88)95/PVMA 5	1.6	38.9	18.2	3.0	33.8	3.7	12.5
534-63	MC + 33% K Acetate	1.4	249.	53.8	1.8	351.	1.7	76.
545-19	MC + 10% Me ₄ NOH	1.3	92.5	61.7	1.6	147.	1.6	98.
499-15	C3	1.6	485.	503.	2.3	536.	2.3	555.

G. Oxidation of Films by Silver Oxide in 30% KOH

It is of interest to examine whether increases in internal resistance of a cell observed with continued cycling could arise from chemical change in the separator. Representative films were set up in 30% KOH, saturated with silver oxide, and allowed to stand for periods ranging from three months to over a year. The Ag_2O -KOH solutions were renewed at least once a month to insure against depletion of dissolved silver oxide. The data summarized in Table VII show that there is a general tendency for resistance to be slowly lowered by continued exposure to the alkaline silver solution. The cellophane and polyvinyl alcohol films were, of course, weakened by the treatment and had to be handled with care.

TABLE VII. Effect of Prolonged Ag_2O Oxidation on Electrolytic Resistance (30% KOH, saturated with Ag_2O)

Reference	Type	Thickness		Days Oxidized	Resistance - milli-	
		Dry mils	Soaked mils		ohms-in. ² original	oxidized
374-61	PUDO Cellophane	1.0	2.9	532	7.6	5.3
	PVAlc (30-98)	1.5	2.7	199	24.7	23.9
	"HEPVA 79" (A)	1.6	2.2	532	23.6	16.0
421-109	E4 (E)	1.6	3.1	522	11.0	8.6
421-66	C1	1.5	2.2	217	72.8	47.5
421-102	C2	1.5	2.4	522	19.0	19.8
421-99	C3	1.5	2.0	98	12.5	8.2
421-95	B3	1.4	2.2	194	12.0	10.4
499-33	MC + 6% KOH	1.5	2.0	212	59.5	51.3
499-75E	C2A (F)	1.5	2.3	211	13.1	12.9
522-140	MC + K Lactate	1.8	2.1	120	348	26.6

Notes: (A) PVAlc (42-88), tetraethylene glycol 22%
 (E) Methyl cellulose 65, hydroxyethyl cellulose 35
 C types are methyl cellulose compositions with PVMA
 B types are methyl cellulose compositions with PAA
 (F) C2 + 10% 3-hydroxypropylamine

H. Stand Time Experiments - Battery of Three Cells Prepared with C3

A battery of three cells prepared at Burgess with C3 separator was submitted to successive stand times of 76, 104 and 174 days and the A.H. capacity determined after each stand period by discharging at C/5 to 1 volt. Charging rate was C/20 to 100% of previous capacity. Data are summarized in Table VIII.

TABLE VIII. - Stand Time Experiments - Battery of C3 Cells

	Stand Time Days	Ampere Hours on Discharge from 1.5 to 1.0 Volt		
		Cell No. 1	Cell No. 2	Cell No. 3
Charged 1/20/66 Discharged 4/6/66	76	8.75	9.00	9.04
Charged 4/6/66 Discharged 7/19/66	104	7.08*	7.08*	7.08*
Charged 7/21/66 Discharged 1/9/67	174	2.31	3.93	1.34

* Not completely discharged. Amperes falling off.

Following the last discharge, the No. 3 cell was disassembled and the silver content of the first and fifth wraps determined. In Table IX the results are compared with silver analyses on separators from two other cells of different history, and from other sources.

TABLE IX. - Distribution of Silver on C3 Separator Wraps

History	mg Ag/sq. inch		
	1st Wrap	2nd Wrap	5th Wrap
Present SS 5.5 Burgess Cell 3 successive stand times	21.7		2.05
Ag/Cd Cell ESB 3 months stand time from J. P. L.	-	8.45	7.82
Ag/Zn Cell after 85 cycles NAD Crane	31.2	-	1.4

In the present experiment the silvered wraps showed a clearly visible gradient in silver distribution from the first to the 5th wrap as was the case for wraps from the Ag/Zn cell after 85 cycles. The cell from JPL, which was shorted after a three months stand period, showed an even distribution of silver from the first to the fifth wrap.

J. Wrapping Electrodes with Separators

In the U-wrapping technique, two silver electrodes are placed butt ends opposing across the lateral dimension of a rectangular separator strip and folded for several wraps in the longitudinal direction. The assembly is then folded at the median line to give a U-bend enclosing the electrodes. This manipulation results in tension at the bend, and in some cases development of cracks, especially in the outer fold. In all cases creases radiate from the point of fold and, no doubt, stresses of unknown magnitude.

Examination of separators from unfilled cells prepared for NASA tests, using our membranes, showed cracks at the fold, even occasionally in the case of cellophane control cells. The most cracks were encountered in the case of a cell prepared with a film in which C1 formulation was modified by the addition of potassium lactate (NAS 5-9107-15, 22), about 30% of the folds showing rupture. To establish whether this occurred from improper conditions of wrapping, electrode forms were carefully wrapped under 50% controlled relative humidity. The incidence of cracking was considerably reduced, rupture occurring, either not at all in the case of the NAS 5-9107-15, 22 and in C3 separator, or in the outside wrap. Nevertheless, it was clear from examination of the wraps that weak points were introduced by the U-wrap technique.

To study this more carefully the separators of principal interest in the current contract were applied as U-wraps and, after a period of a few weeks standing in the folded condition, the films were carefully unwrapped for examination. None of the separators of the current study showed visible holes under a stereomicroscope. However, many showed permanent creases radiating from the fold, particularly in the outer wraps, suggesting incipient cracks. This was particularly observable in the C3 wrap and in the NAS 5-9107-22 film (C1 + lactate).

In an attempt to determine whether physical weaknesses did in fact exist at the folds, tensile strips were cut in the outer wrap portion of the unwrapped separators so that the creased portion was midway in the test strip. Tensile strengths were then measured in comparison to adjacent areas containing no creases. Observations were made of the point of break. Results are shown in Table X.

TABLE X - Effect of Creasing on Tensile Strength of Films

Film	Fold No.	Mils Thick	Creased Samples			Uncreased Samples		
			psi	% elong.	Break at Crease(1)	psi	% elong.	% Strength Retention
C3	2	1.4	8,260	5	+	13,830	6	
(574-60-3)	3	1.4	11,500	2	+	12,330	5	
	4	1.4	8,400	5	+	13,750	7	
			<u>9,387</u>			<u>13,300</u>		70%
MC +	2	1.4	2,025	5	+	3,430	42	
KAc	3	1.4	3,140	25	+	3,640	44	
(574-60-4)	4	1.4	2,785	20	+	3,670	43	
			<u>2,647</u>			<u>3,580</u>		74%
Cl	2	1.3	5,100	5	+	5,950	15	
K Lact.	3	1.3	5,190	18	+	6,340	39	
(574-60-1)	4	1.3	6,460	5	-	6,240	25	
			<u>5,583</u>			<u>6,177</u>		90%
Bl +	2	1.4	7,030	48	-	7,430	60	
K Lact.	3	1.4	7,440	50	hole	7,740	60	
(574-60-7)	4	1.4	7,030	43	-	8,100	62	
			<u>7,167</u>			<u>7,757</u>		92%
MC +	2	1.5	8,780	28	+	10,550	45	
9% KOH	3	1.5	11,200	40	-	9,990	30	
(574-60-5)	4	1.5	7,950	18	-	8,930	26	
			<u>9,310</u>			<u>9,823</u>		95%
PVALc 95	2	1.2	15,800	8	+	16,350	4	
PVALA 5	3	1.2	16,050	8	tear	16,050	(6)	
(574-60-6)	4	1.2	14,800	10	+	15,020	6	
			<u>15,550</u>			<u>15,807</u>		99%
MC +	2	1.4	5,660	22	+	5,740	25	
Me NCH	3	1.4	6,550	40	-	5,690	14	
(574-60-2)	4	1.4	5,410	15	-	6,030	20	
			<u>5,873</u>			<u>5,820</u>		101%

(1) + = broke at crease

- = broke at other locations other than crease.

Test conditions: Span 1"; 2"/min.; 15 mm. wide sample PT 200 L

Reduction in strength appeared to be significantly reduced in only two cases, C3 and the potassium acetate modified methyl cellulose films, although the tendency to break at the crease occurred in most cases.

There is some question as to whether it can without qualification be assumed that the MIT fold test is indicative of a film's ability to withstand wrapping. Correlation with this test has been good especially where cycle numbers below 1000 are found. However, among films of rather good flexibility the lactate modified C1 film (MIT flex 7900) has shown a tendency to be weakened in the electrode wrapping test. Possibly an actual creasing test would be more revealing than the relatively mild action of the MIT test.

One method of relieving stresses in the U wrapping would be to plasticize the critical area, that is the median line along which the final U bend is made. As a groundwork for this approach a number of water-containing compositions which swelled a C3 film without dissolving it were used to test their effect on the flexibility of the film. In parallel experiments these same compositions were painted down the median line of electrode wraps before the electrode forms were U-wrapped. After three days stand the forms were then unwrapped and examined. Results are summarized in Table XI.

TABLE XI. - Effect of Plasticizing Median Line in U-Wrapping
with C3 Separator

Sample	Plasticizer	MIT Flex		Electrode Wraps	
		on Films	Soaked in	Plasticizer Applied Down Median Line	Observations after 3 days
		Plasticizer	Plasticizer	Time After Application	folded
		mil	cycles	min.	
7	None	1.5	470	-	2 small cracks
1	80 TEA/20 H ₂ O	2.3	20,000+	30	no holes
2	90 TEA/10 H ₂ O	2.3	20,000+	30	4 holes
3	80 glycol/20 H ₂ O	2.3	stretched	30	holes at corners, film sticks
4	90 glycol/10 H ₂ O	2.2	stretched	30	holes at corners, 6 cracks
5	100% glycol	2.3	83	30	holes at corners, 6 cracks
6	30% KOH	2.3	20,000+	30	no holes, non-sticky
8	30% KOH	2.3	20,000+	1	1 hole

Notes: TEA is triethanolamine.

From the above it appears that a controlled degree of softening at the median line is worth further study as a possible improvement in the art of wrapping electrodes.

K. Thin Films in Combinations of Two Types

In the silver diffusion experiments of the Second Progress Report it was found that films of polymers of high hydroxyl content such as cellophane, polyvinyl alcohol and hydroxyethyl cellulose are effective barriers for silver ions. The barrier action was shown to be chemical, silver being reduced by the membranes and deposited there as metal.

On the other hand, oxidation-resistant types, as exemplified by methyl cellulose formulations, permitted some diffusion of silver but showed superior performance in field tests in retarding zinc penetration. These findings suggested that a combination of the two types provide a superior separator system for the silver/zinc cell.

An early attempt to apply this principle was the development of the triple laminate film (C3/PVAlc/C3) (NAS 5-9107-5). Although performance in cells of this separator were fairly satisfactory, control difficulties in the manufacture of the films indicated that exact duplication might be quite difficult to achieve. An alternative approach was to include polyvinyl alcohol in a methyl cellulose-polyacid formulation (NAS 5-9107-11) as a homogeneous film. It was found, however, that polyvinyl alcohol so distributed was not efficient as a silver barrier.

The present scheme is based on casting thin films of the two types, superimposing the thin films, and wrapping the electrodes in the double thin films. Thus, films cast at half the usual thickness give alternate layers of the two types without introducing additional separator material. Another advantage to be expected is reduced chance of cracking at the folds because of the much greater flexibility of thin films as shown in Table XII.

TABLE XII. - Effect of Film Thickness on Flexibility

Composition	MIT Flex 200 g. Tension		50% R.H.	
	mils	Cycles	mils	Cycles
C3	0.6	1,865	1.5	754
MC + Me NOH	0.6	14,633	1.5	5,295
Cl + Lactate	0.7	11,411	1.5	3,544
MC + KOHc	0.6	>20,000	1.4	10,340
MC + KOH	0.9	8,534	1.5	2,803

It was pertinent to inquire whether the introduction of additional surfaces would result in a specific resistance greater for a given combination than the addition value for the individual films. Accordingly, a number of potential combinations of the two types of thin films were tested as pairs in the Kelley-Salkind resistance cell as shown in Table XIII. Results generally showed that the combinations gave the additive resistance of the individual films. The tests were made under ideal conditions, that is, the specimen films were equilibrated for three days in the electrolyte and placed quite wet together before being secured in the cell. It was noted, however, that when the soaked specimens were blotted before assembly inordinately high resistances were encountered. It appears, therefore, that complete wetting of the electrode wrap of thin films would be essential to proper performance.

A number of thin film combinations were prepared for cell tests in the Norberg Laboratory. Results will be reported in the Fourth Quarterly Report.

TABLE XIII-a. Resistance of Thin Films, Singly and In Pairs (30% KOH)

Films	Composition	Thickness		Resistance		
		Dry mils	Swollen mils*	ohms-cm based on Swollen Thickness		
				milliohms-in. ² Found	Calc'd.	
574-15	C3 (thick)	1.5	2.54	13.3		13.3
547-19	C3	0.7	1.18	4.56		9.8
574-25	C3	0.7	1.18	5.89		12.7
563-17-6	PVAlc (30-98) (thick)	1.5	2.88	19.00		16.8
574-9	PVAlc (30-98)	0.7	1.33	8.55		16.3
574-28	PVAlc (42-88)	0.8	1.39	10.07		18.4
574-7	PVAlc (42-88)	0.8	1.39	9.12		16.6
574-8	PVAlc (42-88) 95/PVMA 5	0.8	1.58	7.60		12.2
574-21	C3 pH 8 + 5% TEA	0.7	1.06	20.5		49.1
574-22	C3 pH 8 + 5% TEG	0.7	1.06	16.91		40.5
574-20	MC + 28% K Lactate	0.8	.95	40.1		107.
574-26	C1 + 28% K Lactate	0.8	1.08	6.65		15.6
574-50	MC + 28% Me ₄ NOH	0.7	.89	13.3		38.0
574-27	MC + 33% K Acetate	0.7	.84	4.18		12.7
[574-9	PVAlc (30-98)	0.7	1.33	13.87	14.44	13.87]
[574-25	C3	0.7	1.18			
[574-28	PVAlc (42-88)	0.8	1.39	17.29	15.96	17.1]
[574-25	C3	0.7	1.18			
[574-28	PVAlc (42-88)	0.8	1.39	(54.6)	26.99	56.8]
[574-22	C3 pH 8 + TEG	0.7	1.06			
[574-26	C1 + 28% K Lactate	0.8	1.08	17.3	16.72	17.8]
[574-28	PVAlc (42-88)	0.8	1.39			
[574-26	C1 + 28% K Lactate	0.8	1.08	13.1	15.2	13.5]
[574-9	PVAlc (30-98)	0.7	1.33			
[574-27	MC + 33% K acetate	0.7	.84	14.63	14.25	16.6]
[574-28	PVAlc (42-88)	0.8	1.39			
[574-29	PVAlc (42-88) 95/PVMA 5	0.7	1.58	12.92	13.30	12.3]
[574-26	C1 + 28% K Lactate	0.8	1.08			
[574-50	MC + 10% Me ₄ NOH	0.7	.39			
[574-29	PVAlc 95/PVMA 5	0.7	1.59	22.0	26.2	22.6]

*Swollen thickness is calculated from weight of 30% KOH picked up

TABLE XIII-b. Resistance of Thin Films, Singly and In Pairs (45% KOH)

Films	Composition	Thickness		Resistance		
		Dry mils	Swollen mils*	ohms-cm based		
				milliohms-in. ² Found	Calc'd. Thickness	on Swollen Thickness
499-65	PVAlc (thick)	1.5	2.88	31.5		27.8
574-9	PVAlc (30-98)	0.7	1.73	10.1		14.8
574-14	PVAlc (30-98)	0.7	1.73	9.7		14.2
574-28	PVAlc (42-88)	0.8	1.76	7.5		10.8
574-7	PVAlc (42-88)	0.8	1.76	8.9		12.8
574-8	PVAlc (42-88) 95/PVMA 5	0.8	1.97	7.2		9.3
574-29	PVAlc (42-88) 95/PVMA 5	0.7	1.72	6.4		9.5
574-19	C3	0.7	1.18	240.		520.
574-25	C3	0.7	1.18	294.		634.
574-15	C3 (thick)	1.5	2.54	368.		368.
574-21	C3 pH 8 + 5% TEA	0.7	1.18	48.6		104.
574-22	C3 pH 8 + 5% TEG	0.7	1.18	41.4		89.
574-27	MC + 33% K Acetate	0.7	.82	4.6		14.3
574-20	MC + 28% K Lactate	0.8	.94	170.0		460.
574-18	C1 + 28% K Lactate	0.8	1.10	9.1		21.0
574-26	C1 + 28% K Lactate	0.8	1.10	8.9		20.5
574-50	MC + 10% Me ₄ NOH	0.7	.94	22.2		60.
574-9	PVAlc (30-98)	0.7	1.73	216.	304	189.
574-25	C3	0.7	1.18			
[574-28	PVAlc (42-88)	0.8	1.76	248.	302.	214.]
[574-25	C3	0.7	1.18			
[574-29	PVAlc (42-88) 95/PVMA 5	0.7	1.72	23.0	15.3	28.6]
[574-26	C1 + 28% K Lactate	0.8	1.10			
[574-28	PVAlc (42-88)	0.8	1.76	167.	178.	149.]
[574-20	MC + 28% K Lactate	0.8	1.10			
[574-28	PVAlc (42-88)	0.8	1.76	23.	16.4	20.4]
[574-26	C1 + 28% K Lactate	0.8	1.10			
[574-28	PVAlc (42-88)	0.8	1.76	19.2	12.1	18.5]
[574-27	MC + 33% K Acetate	0.7	.82			
[574-28	PVAlc (42-88)	0.8	1.76	45.2	48.9	39.2]
[574-22	C3 PH 8 + 5% TEG	0.7	1.18			
[574-50	MC + 10% Me ₄ NOH	0.7	.94	40.3	28.6	109.]
[574-29	PVAlc 95/PVMA 5	0.7	1.72			

*Swollen thickness is calculated from weight of 45% KOH picked up.

ITEMS OF NEW TECHNOLOGYI. PRE-COOLING MEMBRANES TO INCREASE THEIR CONDUCTIVITY

Pre-cooling a methyl cellulose membrane at below -55°C . in 30% potassium hydroxide solution lowered the resistance of the membrane at room temperature from 590 to 60 milliohms-in.² The low resistance persisted over a 134 day period. Increased swelling and increased diffusion rate for silver were also brought about by the pre-cooling cycle.

Application of a similar pre-cooling cycle to compositions in which methyl cellulose is modified by polar additives can result in still greater decreases in resistance, even to levels lower than that of cellophane. Since silver diffusion rate would be correspondingly high, such films by themselves might not be appropriate for use in secondary Ag/Zn or Ag/Cd cells. Study of their use in layered combinations with films which scavenge silver is recommended. Investigation in other types of cells, such as zinc-oxygen, is also recommended.

II. PRE-SOAKING MEMBRANES IN LESS CONCENTRATED ALKALI
TO IMPROVE THEIR CONDUCTIVITY IN CONCENTRATED ALKALI

Pre-soaking methyl cellulose membranes in 15% KOH not only lowers their electrolytic resistance in either 30% or 45% KOH, but also increases swelling and permeation to silver ion. Application of this pre-soaking procedure to compositions in which methyl cellulose is modified by polar additives can result in still greater changes. Electrolytic resistance can be decreased to levels lower than that of cellophane. Since silver diffusion rate would be correspondingly high, such films by themselves might not be appropriate for use in secondary Ag/Zn or Ag/Cd cells. Study of their use in layered combinations with films which scavenge silver is recommended. Investigation of other types of cells, such as zinc-oxygen, is also recommended.

III. METHYL CELLULOSE-TETRAMETHYLAMMONIUM HYDROXIDE COMPOSITION FOR FILMS

Flexible films which had excellent conductivity in 45% potassium hydroxide were prepared with the composition one part tetramethyl ammonium hydroxide to ten parts methyl cellulose. MIT flex of the dry film was greater than 4000 cycles at 50% R.H. Electrolytic resistance in 45% KOH was 54 ± 8 ohms-cm. Preliminary evaluation in Ag/Zn cells was promising.

ITEMS OF NEW TECHNOLOGY (CONTINUED)IV. BUFFERING METHYL CELLULOSE-POLYACID FILMS TO IMPROVE CONDUCTIVITY

The resistance in 45% KOH of C3 films is lowered from 500 to 19 milliohms-in.² by casting the film from aqueous solution buffered with KOH to pH 8. Silver diffusion rate is concomitantly increased three-fold. Practicality of these buffered films is for the present limited by difficulties in their manufacture.

V. SEPARATOR FILMS FROM METHACRYLATE-ACRYLATE COPOLYMERS

Films may be made from certain copolymers of methacrylate esters with substituted ammonium acrylates. These films are sufficiently flexible to be handled in operations such as wrapping electrodes. Electrolytic resistances vary with polymer composition. Values as low as for cellophane in 30-40% KOH can be reached, but silver diffusion is then correspondingly high. The copolymers are prepared by selective hydrolysis of copolymers of methacrylate esters with acrylate esters, followed by partial or complete neutralization of the resultant acrylic acid copolymer by addition of an amine base.

VI. PREPARATION OF NON-CRACKING U-WRAPS FOR ALKALINE BATTERY CELLS

When the U-bend technique is used to wrap separator membranes around electrodes, it has been observed that even relatively flexible films sometimes exhibit a tendency to crack at the U-bend if not handled with excessive care. An effective way of decreasing the chance of such damage has been found to be the prior application of electrolyte solution to the area to be stressed. Other plasticizing solutions might serve the same purpose, but electrolyte solution has the advantage of substantially adding nothing to the final assembly.